

Dipole moment and molecular polarization of some alcohols in carbontetrachloride solutions

S L Abd-El Messieh, A L G Saad and K N Abd-El-Nour

Department of Microwave Physics, National Research Centre, Dokki, Cairo, Egypt

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Abstract The dipole moments μ of some normal, iso, and cyclo alcohols and their binary mixtures have been determined in dilute and concentrated solutions of carbon tetrachloride at 20, 30 and 40 °C. The inflection point at which the associates possess a considerably high polarization and the dipole moment increases continuously with the increase in concentration, was obtained and the shift was discussed according to those associates. At a certain dipole concentration N , a common region of intersection was noticed referring to some sort of isoelectric behaviour.

The apparent equilibrium constants K of such alcohols at 20 °C have been determined using the method of Few and Smith. The data obtained are interpreted according to the degree of association which is induced by the hydroxyl groups.

Keywords : Dipole moment, molecular polarization, equilibrium constant.

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1. Introduction

Dielectric investigations of hydrogen-bonded compounds in non-polar solvents provide valuable information regarding molecular complex formation in solution.

Many static permittivity measurements have been carried out on dilute and concentrated solutions of some normal [1,2] and iso-alcohols [3] in non-polar solvents. It revealed an interesting behaviour in which the curves of the dipole moment at the various temperatures versus concentration intersect at a certain region of concentration N .

From the dielectric polarization measurements, series of studies were carried out to evaluate quantitatively the apparent equilibrium constant K for the complexes formed either from donor-acceptor systems [4,5] or from associating molecules having hydroxyl groups [6,7].

So, it seems interesting to carry out systematic investigations and measure the static permittivity and dielectric polarization for some short and long chain alcohols and their binary mixtures as well as their iso- and cyclic- isomers in an inert non-polar solvent carbon-tetrachloride, in order to study the association phenomena in such alcohols.

2. Experimental

(i) Techniques :

The dielectric measurements at low frequency (2 MHz) were done using a dipolemeter (type DMO1 from Wiss. Techn. Werkstaten GMBH (WTW), Germany) with experimental error amounting to 0.5%. The measuring cell, (type DFL1) was used and maintained at the testing temperatures 20°, 30° and 40°C by circulating water from an ultrathermostat through a jacket surrounding the cell used.

An Abbé refractometer (Carl Zeiss Jena, Germany, Model G) was used to measure the refractive index n_D of Na-D line to an accuracy of $\pm 1 \times 10^{-4}$.

The density was measured using 10 ml specific gravity bottle.

(ii) Materials :

The alcohols used were obtained from BDH, England, while carbontetrachloride which was used as a solvent was supplied by Merck, Germany. All chemicals were used as received.

3. Results and Discussion

(i) Dipole moment measurements :

The static permittivity ϵ_0 , refractive index n_D and density ρ were measured for dilute and concentrated solutions of two normal alcohols, propanol (C_3) and heptanol (C_7), and their mixtures with ratios 1:3, 1:1 and 3:1 in CCl_4 at 20°, 30° and 40°C. The measurements were also carried out for n-butanol (C_4) and isobutanol and for n-hexanol and (C_6) and cyclohexanol.

The dipole moment μ for the dilute solutions with concentration x not exceeding 6 mole %, was determined from the Guggenheim equation [8] :

$$\mu^2 = \frac{27KTM}{4\pi N_A \rho} \cdot \frac{(\Delta\epsilon_0 - \Delta n_D^2) / x}{(\epsilon_s + 2)^2},$$

M , ρ and ϵ_s are the molecular weight, density and permittivity of the solvent ; N_A is Avogadro's number, $\Delta\epsilon_0$ and Δn_D^2 are the differences in the static permittivity and the square of refractive index between solution and solvent.

For concentrated solutions and pure substances, the dipole moment was calculated using Onsager's Equation[9],

$$\mu^2 = \frac{9KT}{4\pi N} \cdot \frac{(\epsilon_0 - n_D^2)(2\epsilon_0 - n_D)}{\epsilon_0 (n_D^2 + 2)^2},$$

ϵ_0 and n_D are the static permittivity and refractive index of the solutions ; N is the number of dipoles per unit volume and equals to $\frac{N_A \rho}{\bar{M}} x$, $\bar{\rho}$ and \bar{M} are the density and molecular weight of the solution.

The values of μ obtained for all investigated molecules using both equations, are illustrated graphically in Figures (1-3) versus the number of dipoles per $Cm^3(N)$. From these

figures, it is noticed that at very low concentrations, the values of μ decrease by increasing the number of dipoles. This decrease may be due to the formation of an associate, less polar than the monomer. This region is followed by an equilibrium between the monomer and its less polar associate in the solution, as μ remains constant through a limited range of concentration. An

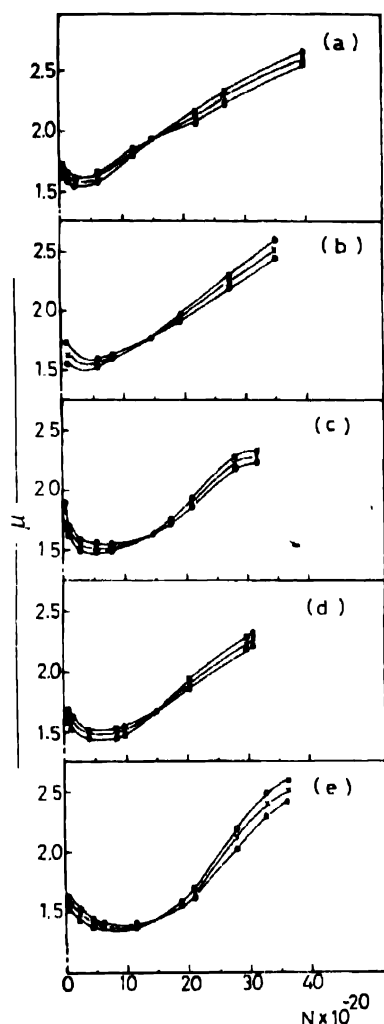


Figure 1. Dipole moment μ in Debye units versus number of dipoles/ Cm^3 (N) for (a) *n*-propanol C_3 , (e) *n*-heptanol C_7 , and their mixtures with notations (b) 3:1 (c) 1:1 and (d) 1:3, in CCl_4 at 20°C (○), 30°C (×) and 40°C (●)

inflection point occurs beyond which the associates possess considerably higher polarity and the dipole moment increases continuously with the increase in concentration. This behaviour was interpreted according to Kirkwood factor g of most normal alcohols [10] by the fact that hydrogen bond association favours cyclic multimers at low concentrations and open multimers at high concentrations. The values of the inflection point (dip) obtained from Figures (1-3) are listed in Table I.

Table 1. Inflection point (dip) ($N \times 10^{20} \text{ cm}^{-1}$) of the different investigated alcohols at 20°C.

Alc.	<i>n</i> -C ₃	C ₃ +C ₇ 3.1	C ₃ +C ₇ 1.1	C ₃ +C ₇ 1.3	<i>n</i> -C ₇	<i>n</i> -C ₄	iso-C ₄	<i>n</i> -C ₆	Cyclo C ₆
N	2.3	3.5	5.6	6.5	9.0	2.5	5.5	3.5	8.5

From this table, it is noticed that the inflection point (dip) of $\text{C}_7 > \text{C}_3$ while the mixtures of $\text{C}_7 + \text{C}_3$ are in between. On the other hand, $n\text{-C}_4$ is found to be lower than iso- C_4 and $n\text{-C}_6$ is lower than cyclo- C_6 .

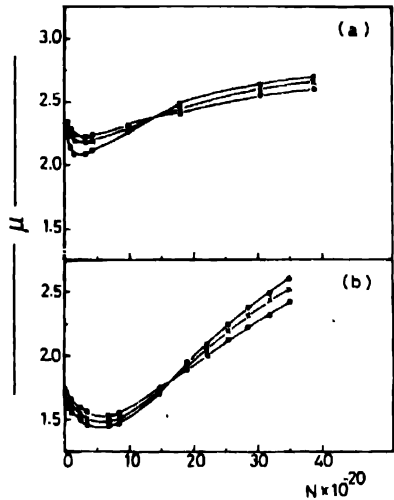


Figure 2. Dipole moment μ in Debye units versus number of dipoles / Cm^3 (N) for (a) n -butanol C_4 and (b) iso-butanol in CCl_4 at 20 °C, 30 °C and 40 °C.

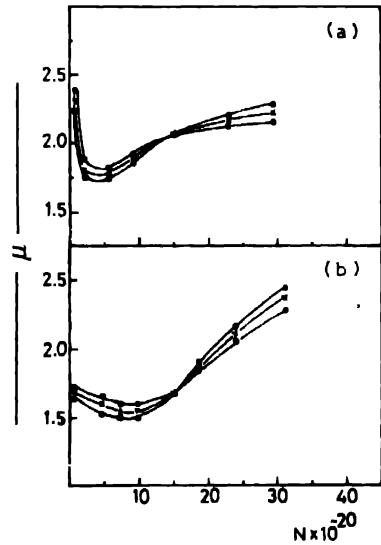


Figure 3. Dipole moment μ in Debye units versus number of dipoles / Cm^3 (N) for (a) n -hexanol C_6 and (b) cyclohexanol in CCl_4 at 20 °C, 30 °C and 40 °C.

At $N = 15 \times 10^{20} \text{ cm}^{-3}$, some sort of isoelectric behaviour could occur which leads to a point of intersection of all curves at the different temperatures. Below this point the dipole moment increases with increasing temperature, while above this point it decreases. The qualitative explanation of the behaviour below $N = 15 \times 10^{20} \text{ cm}^{-3}$ could be due to intermolecular association into ring and linear dimers and μ increases with the increase in temperature. At $N = 15 \times 10^{20} \text{ cm}^{-3}$, some sort of isoelectric behaviour occurs and a ring chain equilibrium exists such that the temperature has no effect on μ . Beyond this concentration, μ is decreasing with higher temperatures and increasing with higher concentrations, indicating that big chain associates are formed.

It is also interesting to find that this point is about the same for all types of investigated alcohols, either single or mixed alcohols. This result is comparable with that found before [3] in case of isopropanol and isobutanol and their binary mixtures in CCl_4 and cyclohexane ($N \cong 16 \times 10^{20} \text{ cm}^{-3}$) while it is $11 \times 10^{20} \text{ cm}^{-3}$ in case of decalin. This indicates that the intersection point is independent of the type of the alcohol used whatever the morphology is, while it is dependent on the solvent used.

(ii) Dielectric polarization measurements :

The intermolecular associates which are expected to be formed in the investigated alcohols have been studied quantitatively by means of dielectric polarization measurements. These measurements were conducted using the method of Few and Smith [11]. This method was developed to relate the apparent equilibrium constant K of the association process and the molecular polarization of the complex P_{AB} through the following equation

$$\frac{\Delta P}{P_A^* - P_A} = 1 + \frac{M_B}{K W_B d}$$

where P_A is the molecular polarization at infinite dilution of the alcohol A in a constant-ratio mixture of alcohol B and the inert non-polar solvent S ; P_A^* is the molecular polarization at infinite dilution of the alcohol A in the non-polar solvent S ; $\Delta P = P_{AB} - P_A - P_B$ is the increase in the molecular polarization at infinite dilution associated with the formation of 1 mole of association complex AB from the alcohol A and the alcohol B ; W_B is the weight fraction of the alcohol B ; d is the density of the alcohol – solvent mixture BS . To carry out such study, three series of systems were chosen :

(a) *n*-Propanol (C_3) and *n*-Heptanol (C_7) Systems :

Five mixtures of different concentrations of C_3 (B) in CCl_4 (S) were prepared having mole fractions between 0.0079 and 0.057. A series of dilute solutions of C_7 (A) in each of these constant-ratio solvent mixtures BS were prepared by weight. All mixtures were left to stand at room temperature (25°C) for 24 hours to attain equilibrium before measurements.

The same steps were also done by considering C_7 as the alcohol B while C_3 is the alcohol A . The results obtained for these two systems are given in Table 2. A plot of $1/(P_A^* - P_A)$ versus $1/(W_B d)$ gives a straight line. The slope of this line gives the value of K while the intercept with the Y -axis gives ΔP . The values obtained for K and ΔP are listed in Table 2. From this table, it is noticed that the values of K and ΔP are higher for propanol than for heptanol indicating that propanol is more associated than heptanol i.e. $C_3 > C_7$. This could be attributed

to the number of dipoles per unit volume which is supposed to be larger in the case of propanol.

Table 2. Polarization data of (A) *n*-heptanol in the presence of *n*-propanol (B) *n*-heptanol in the presence of tertbutylchloride, (C) *n*-propanol in the presence of *n*-heptanol, (D) *n*-propanol in the presence of tertbutylchloride

W_B	d_{BS} g/cm ³	P_A^*	$1/(P_A^* - P_A)$	$1/W_B d_{BS}$	ΔP C C	K L/mol
(A)						
0.000	1.6000	19.46				
0.004	1.5971	22.35	0.346	164.77		
0.016	1.5875	28.84	0.107	38.41	25.86	2.41
0.032	1.5755	32.45	0.077	19.71		
0.051	1.5611	35.55	0.062	12.51		
0.067	1.5495	36.74	0.058	9.70		
(B)						
0.000	1.6000	30.53				
0.005	1.5959	33.25	0.368	118.23		
0.015	1.5884	36.89	0.157	41.47	21.27	2.00
0.033	1.5749	40.70	0.098	19.24		
0.046	1.5647	42.46	0.084	13.77		
0.068	1.5483	43.97	0.074	9.50		
(C)						
0.000	1.6000	32.83				
0.008	1.5940	47.09	0.070	79.41		
0.015	1.5886	50.08	0.058	41.97	28.15	4.64
0.023	1.5825	52.62	0.051	27.47		
0.037	1.5715	55.66	0.044	16.98		
0.057	1.5566	60.00	0.037	11.25		
(D)						
0.000	1.6000	30.53				
0.015	1.5886	47.48	0.059	43.11		
0.031	1.5761	51.80	0.047	20.47	27.3	4.20
0.045	1.5653	53.30	0.044	14.17		
0.061	1.5528	54.30	0.042	10.51		
0.103	1.5210	55.53	0.040	6.36		

This study was extended to evaluate K and ΔP for propanol and heptanol by replacing the alcohols which were added at infinite dilution by unassociated rigid material, tertbutyl chloride. Same steps were done to carry out the dielectric polarization measurements concerning C_3 and C_7 as B and rigid molecule (tertbutyl chloride) as A . The results obtained for these two systems are also given in Table 2. From this Table, it is clear that the values of K and ΔP in the presence of tertbutyl chloride are considerably less than those obtained in the presence of other alcohols but still $C_3 > C_7$. This could be attributed to tertbutyl chloride which may have a negligible effect on the association phenomena in comparison with alcohol even if it is added at infinite dilution.

(b) n-butanol (C₄) and iso-butanol systems :

The associates which are supposed to be formed in normal and iso-butanol were studied using the same procedure as above taking in the beginning *n*-butanol as alcohol *B* and iso-butanol which was added at infinite dilution as alcohol *A*. The same steps were repeated by considering isobutanol as alcohol *B* and butanol as alcohol *A*.

The data obtained for both systems are given in Table 3. The values of *K* and ΔP given in this table indicate that *n*-butanol is more associated than iso-butanol. This could be attributed to the shielding effect which may be imparted by the isomer configuration of the butanol structure. The same trend is also obtained by replacing the added alcohols by tertbutyl chloride. *K* and ΔP given in Table 3 indicate that *n*-butanol and iso-butanol show lower values in the presence of the rigid molecule.

Table 3. Polarization data of (A) isobutanol in the presence of *n*-butanol, (B) isobutanol in the presence of tertbutylchloride, (C) *n*-butanol in the presence of isobutanol, (D) *n*-butanol in the presence of tertbutylchloride

W_B	d_{BS} g/cm ³	P_A^*	$1/(P_A^* - P_A)$	$1/W_B d_{BS}$	ΔP C C	<i>K</i> L/mol
(A)						
0.000	1.6000	12.02				
0.003	1.5916	15.34	0.301	209.40		
0.013	1.5840	22.12	0.099	50.14	28.32	3.22
0.038	1.5638	29.56	0.057	16.83		
0.061	1.5456	32.85	0.048	10.61		
0.087	1.5249	34.74	0.044	7.54		
(B)						
0.000	1.6000	30.53				
0.020	1.5848	45.45	0.067	31.55		
0.030	1.5765	48.07	0.057	21.14	26.20	3.10
0.040	1.5682	49.76	0.052	15.94		
0.060	1.5530	51.36	0.048	10.73		
0.090	1.5348	52.75	0.045	7.24		
(C)						
0.000	1.6000	9.37				
0.013	1.5893	24.68	0.065	46.96		
0.025	1.5802	28.66	0.052	25.42	28.07	4.17
0.052	1.5583	32.24	0.044	12.25		
0.065	1.5486	33.30	0.042	9.98		
0.087	1.5354	34.09	0.041	8.01		
(D)						
0.000	1.6000	30.53				
0.025	1.5811	49.05	0.054	25.30		
0.044	1.5666	51.80	0.047	14.51	27.00	4.00
0.057	1.5557	53.26	0.044	11.28		
0.072	1.5454	53.79	0.043	8.99		
0.120	1.5128	54.92	0.041	5.51		

(c) *n*-hexanol (C_6) and cyclohexanol systems :

As the study of cyclic compounds is considered to be important due to their physiological and industrial applications, it seems interesting to discuss the association of cyclohexanol in comparison to *n*-hexanol. This study has been carried out through the calculation of K and ΔP for the systems containing the corresponding alcohols and the rigid molecule. The values of K and ΔP given in Table 4 for both investigated alcohols in the presence of the other alcohols are found to be higher than those in the presence of the rigid molecule which may have a negligible contribution on the association phenomena. The data given in this table also indicate that *n*-hexanol is more associated than cyclohexanol even if the increase in association does not exceed 15 % for the apparent equilibrium constant K .

Table 4. Polarization data of (A) cyclohexanol in the presence of *n*-hexanol (B) cyclohexanol in the presence of tertbutylchloride, (C) *n*-hexanol in the presence of cyclohexanol, (D) *n*-propanol in the presence of tertbutylchloride

W_B	d_{BS} g/cm ³	P_A^*	$1/(P_A^* - P_A)$	$1/W_B d_{BS}$	ΔP C C	K L/mol
(A)						
0.000	1.6000	62.03				
0.014	1.5894	71.04	0.111	44.94		
0.027	1.5791	74.80	0.078	23.45	24.99	2.58
0.044	1.5658	77.96	0.063	14.51		
0.056	1.5562	79.25	0.058	11.48		
0.063	1.5507	79.90	0.056	10.23		
(B)						
0.000	1.6000	30.53				
0.012	1.5906	37.03	0.154	52.39		
0.027	1.5793	41.47	0.092	23.45	23.24	2.08
0.044	1.5654	44.16	0.074	14.52		
0.049	1.5617	44.62	0.071	13.07		
0.053	1.5586	44.99	0.069	12.11		
(C)						
0.000	1.6000	32.29				
0.010	1.5922	40.87	0.132	62.81		
0.020	1.5844	44.30	0.090	31.56	24.10	2.91
0.034	1.5734	48.02	0.068	18.69		
0.052	1.5590	50.10	0.060	12.34		
0.063	1.5507	51.30	0.056	10.24		
(D)						
0.000	1.6000	30.53				
0.013	1.5899	38.05	0.133	48.38		
0.019	1.5852	40.08	0.105	33.20	22.86	2.43
0.031	1.5761	42.86	0.081	20.47		
0.044	1.5656	44.70	0.071	14.52		
0.061	1.5523	46.30	0.063	10.56		

To sum up the data of K and ΔP given in Tables (2-4) for normal alcohols, it is noticed that both parameters show an increase in the order C_3 , C_4 , C_6 and C_7 . This indicates that short alcohols are more associated than long ones as the number of dipoles N which occupy the unit volume of solution, is larger. The data of N obtained at 20°C are found to be 83, 67, 49 & 44 $\times 10^{20} \text{ cm}^{-3}$ at 20°C for C_3 , C_4 , C_6 and C_7 respectively.

On the other hand, it is interesting to notice that K and ΔP for the investigated normal alcohols increase irregularly with increase in the number of carbon atoms *i.e.* C_3 and C_4 are found to be much higher than C_6 and C_7 . This is in accordance with what had been obtained before [12,13] where the relaxation times for butanol (C_4) and its mixtures with non-polar solvents behave contrary to what was found in case of the long chain alcohols and their mixtures. From this study, it can be concluded that the association phenomena for the short chain alcohols are different from those for the long ones even if they are more associated.

4. Conclusion

According to the values of the inflection points given in Table 1 in comparison to the trend of the equilibrium constant K given in Tables (2-4) for all investigated alcohols, it is interesting to notice that for the strong associated alcohols, the position of the inflection point is extended to lower values of the dipole concentration N . This leads to the conclusion that as the dielectric polarization method is well suited to determine the degree of association, the shift in the inflection points might be taken as a confirmation for the association study.

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